Effect of silicon microstructure on stress - stimulated creation of thermal donors

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ABSTRACT

Effect of intentionally created oxygen - related structural defects on generation of thermal donors, TD's, in Cz-Si treated at (670 K) 720 K under enhanced hydrostatic pressure of gas ambient, HP, up to 1.5 GPa (HT - HP treatment) was investigated. The as - grown Cz-Si samples with initial interstitial oxygen content up to $1.2x10^{18}$ cm^{-3}, as well as that pre - annealed at 720 - 1020 K - 10^5 Pa for up to 170 h, indicate strongly HP - dependent increase of electron concentration in the conduction band after the HT - HP treatment at 720 K for 2 - 20 h. This confirms the stress - stimulated creation of TD's. HP - induced creation of TD's was much weaker after pre - annealing at 920 - 1020 K while not detected for the samples containing extended defects (created by 2 - steps pre - annealing at 10^5 Pa, the second step at 1230 - 1420 K). Qualitative explanation of observed phenomena was proposed.

Keywords: Cz-Si, microstructure, defects, thermal donors, annealing, hydrostatic pressure, oxygen interstitials.

1. INTRODUCTION

The nature of thermal donors in Czochralski silicon crystals, Cz-Si (the basic semiconductor for microelectronics), created in effect of annealing at 670 - 720 K (thermal donors, TD's) and at 870 - 1000 K (new donors, ND's) is still not fully understood. Enhanced hydrostatic pressure, HP, of neutral gas ambient at annealing (HT - HP treatment) of as - grown Cz-Si as well as of that pre - annealed at 720 K result in the much higher (even for an order of magnitude as compared to that observed for the samples annealed at 10^5 Pa) rate of TD's and ND's generation[1-7]. The presence of HP - induced TD's and of ND's is also manifested by deep - level photoluminescence at about 1.08 eV detected at 2 K whereas the PL peak at 0.79 eV has been observed at room temperature[8]. Creation of thermal double donors[9], TDD's, with ground state binding energies 42 - 57 meV was confirmed[7] in the HP - treated Cz-Si samples by Fourier Transform Infrared Spectroscopy, FTIR. On the other hand, generation of shallow thermal donors with ionization energies of 30 - 40 meV was reported for such samples (interpretation of photoconductivity measurements)[5].

One possible explanation of stress - stimulated creation of thermal donors is related to HP - induced activation of initially existing structural irregularities, that act at HT - HP as the nucleation centres for growth of oxygen clusters exhibiting donor activity[4,7]. Just this presumption is investigated in the present work in more details.

The Cz-Si samples with oxygen interstitials, O_i, concentration, c_o, up to above $1.1x10^{17}$ cm^{-3} were subjected to one or two - steps pre - annealing at 10^5 Pa (atmospheric pressure) to cause oxygen precipitation and creation of different oxygen - related defects (what follows as well in decrease of c_O) . Such pre - annealing results in creation of „additional" local irregularities in oxygen distribution. The as - grown (reference) and pre - annealed samples were next subjected to the HT - HP treatment at 670 / 720 K under hydrostatic pressure up to 1.5 GPa and their structural and electrical properties were determined.

2. EXPERIMENTAL

The (001) oriented 100 mm Cz-Si wafers from different suppliers, with c_o up to above $1.1x10^{17}$ cm^{-3} and of different conductivity (Table 1) were subjected to pre - annealing at T = 720 - 1420 K in nitrogen for up to 170 h, eventually followed by the next pre - annealing step at 1230 K or 1420 K, to create oxygen clusters and other oxygen - related defects. The samples of about 10 x 10 x 0.6 mm^3 dimension were cut from the pre - annealed wafers and treated

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Intl. Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals, Antoni Rogaski, Krzysztof Adamiec, Pawel Madejczyk, Editors, Proceedings of SPIE Vol. 4412 (2001) © 2001 SPIE · 0277-786X/01/$15.00

Table 1. Typical investigated samples: designation, supplier, initial conductivity type, carrier concentration, N_i, and O_i concentration, c_o.

Sample designation	Supplier	Type	N_i x 10^{15}, cm^{-3}	c_o x 10^{17}, cm^{-3}
A	Silicon - IEMT	p	0.8	6.2
B	Silicon - IEMT	n	1.0	6.5
C	Silicon - IEMT	n	0.9	8.0
D	Silicon - IEMT	p	0.85	8.0
E	Silicon - IEMT	p	1.9	10.8 - 11.8
F	Russia	n	1.2	6.8
G	Russia	p	1.1	7.0
H	Wacker	n	1.0	9.2

at 670 K / 720 K under argon pressure up to 1.5 GPa for up to 20 h in high pressure furnace. Kind and density of defects created at pre - annealing were revealed by optical observation after selective etching in the Yang solution. After the HT - HP treatment about 20 μ thick sample surface layer was removed to prepare the samples for electrical (CV, four point probe methods), and FTIR (conversion factor equal to 2.45 was used to calculate c_o) measurements.
Most results are reported for the samples treated at temperature 720 K, at which the TD's creation rate was the highest. In what follows the conditions of pre-annealing (T and time) are indicated in parenthesis after the sample symbol.

3. RESULTS

3.1 Effect of HT - HP treatment on carrier concentration in as - grown (reference) Cz-Si

Effect of HT - HP treatment on carrier concentration (related to creation of TD's) in as - grown (reference) Cz-Si samples is presented in Figs 1 and 2 (for sample designations see Table 1). $\Delta N_e = |N_{HT\text{-}HP} - N_i|$, where $N_{HT\text{-}HP}$ means the carrier (electron) concentration after the HT-HP treatment and N_i - the initial carrier concentration (see Table 1).

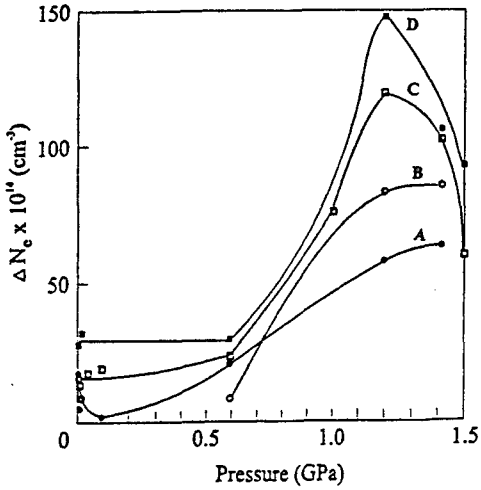

Fig. 1. Dependence of ΔN_e on HP for A, B, C, and D samples treated for 10 h at 720 K - HP.

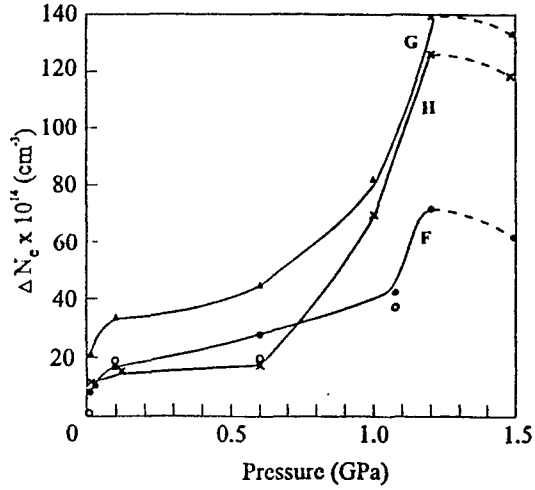

Fig. 2. ΔN_e for F, G and H samples treated at 720K- HP for 10 h, as determined by CV and Hall measurements (the last marked by o).

Table 2. ΔN_e (x10^{15}, cm^{-3}) after the treatments at 670 K - 1.2 GPa - 10 h and 720 K - 1.2 GPa - 10 h.

Sample:	A	B	C	E	F	G	H
$\Delta N_{e\,670K}$:	1.5	1.1	2	4.4	1.1	3.6	1.5
$\Delta N_{e\,720K}$:	6	8.5	11.6	16	7	13.5	12.5

The ΔN_e value peaks for HP equal to about 1.1 - 1.3 GPa for treatment time equal to 10 h (Figs 1, 2). The ΔN_e „peak" values measured for the samples treated at 670 K - 1.2 GPa and 720 K - 1.2 GPa for 10 h are compared in Table 2.

3. 2. Effect of pre - annealing on carrier concentration in Cz-Si treated at 670 / 720 K - HP

Interstitial oxygen concentration and density of defects, d, revealed in chosen pre - annealed (at 720 - 1000 K - 10^5 Pa) samples (of stacking faults, SF, precipitate dislocation complexes, PDC, and saucer pit defects, SPD) are presented in Table 3.

Table 3. Microstructure of some pre - annealed samples (before the treatment at 670 - 720 K - HP).

Sample	Pre-annealing [K, h]:	c_ox10^{17}, cm^{-3}	d_{SF}, cm^{-2}	d_{PDC}, cm^{-2}	d_{SPD}, cm^{-2}
E	720K-10h	11.3	-	$2x10^3$	$2x10^5$
E	720K-40h	10	-	$4x10^3$	$5x10^3$
G	720K-170h	6.8	-	-	$5x10^4$
E	920K-10h	11.7	-	$4x10^2$	$3x10^3$
E	920K-20h	11.8	$4x10^2$	-	$3x10^3$
E	720K-20h+820K-20h	9.8	$2.5x10^6$	$2x10^2$	$2x10^2$
E	1000K-20h	8.5	$4x10^2$	$3x10^5$	$1x10^6$

The ΔN_e values measured for the samples treated at 670 K - 1.2 GPa and 720 K - 1.2 GPa for 10 h are compared in Table 4. Effect of pre - annealing at 10^5 Pa on carrier concentration in Cz-Si treated at 720 K - 1.2 GPa for up to 20 h is presented in Fig 3.

The samples pre - annealed for prolonged time (for 40 h - sample E and for 170 h - sample G) at 720 K - 10^5 Pa (typical conditions for creation of TD's at ambient pressure) exhibit further rise of electron concentration in the conduction band if next treated at 670 - 720 K under HP (compare ΔN_e dependence on treatment time for samples G and G (720 K - 170 h). The same (but to a lesser extent) concerns the samples subjected to pre - annealing at 920 K and 1020 K for up to 40 h.

Dependencies of ΔN_e on HP for the C and E samples subjected to pre - annealing at 720 K, 920 K and 1000 K and afterwards treated at 720K - HP are presented in Fig. 4.

Changes of the interstitial oxygen concentration in effect of the treatment at 720 K / 870 K - HP are presented in Fig. 5. Results for treatment temperature equal to 870 K were presented to stress an effect of the treatment temperature on oxygen precipitation which also occurs during annealing / treatment.

Table 4. ΔN_e (x10^{15}, cm^{-3}) measured for samples subjected to pre - annealing and afterwards treated at 670 K - 1.2 GPa - 10 h and 720 K - 1.2 GPa - 10 h.

Sample:	C(720K-20h)	E(720 K-10h)	E(720K-40h)	E(920K-10h)	G(720K-170h)
$\Delta N_{e\,670K}$:	5.4	5.4	10.4	3.4	8.1
$\Delta N_{e\,720K}$:	7.6	17	18.6	20	11.3

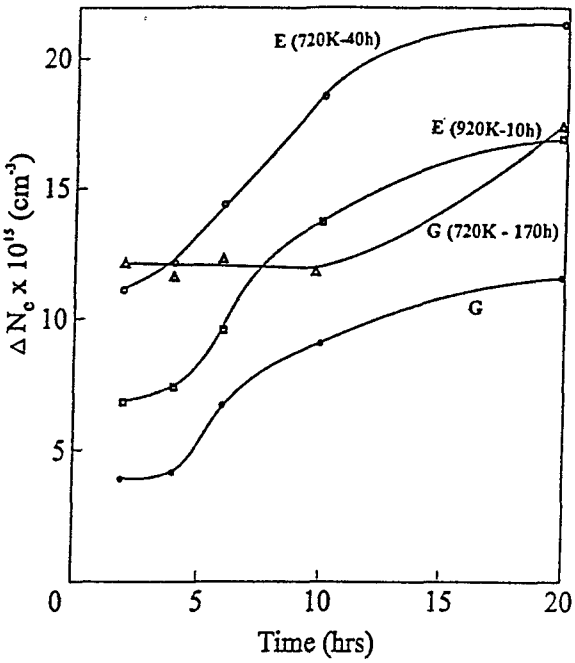

Fig. 3. ΔN_e dependence on time of treatment for pre-annealed E and G samples treated at 720 K - 1.2 GPa and for as - grown reference G sample.

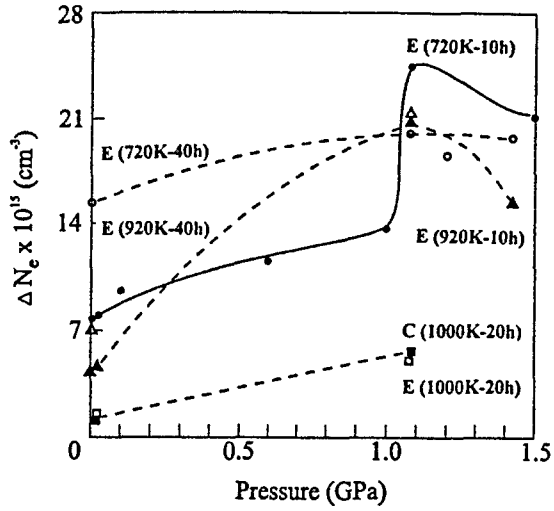

Fig. 4. ΔN_e dependence on HP for C and E samples pre-annealed at 720 K, 920 K and 1000 K and afterwards treated at 720 K - HP for 10 h.

The most „pressure - sensitive" (in respect of the highest values of ΔN_e) were the E samples with the highest content of interstitial oxygen, as - grown ($\Delta N_e = 1.58 \times 10^{16}$ cm^{-3} after the treatment at 720 K - 1.2 GPa for 20 h), and that pre - annealed at 720 K - 10^5 Pa (Figs 3, 4). In effect of the HT - HP treatment an increase of electron concentration in the conduction band occurs with simultaneous decrease of the interstitial oxygen concentration (Table 3, Fig. 5, compare

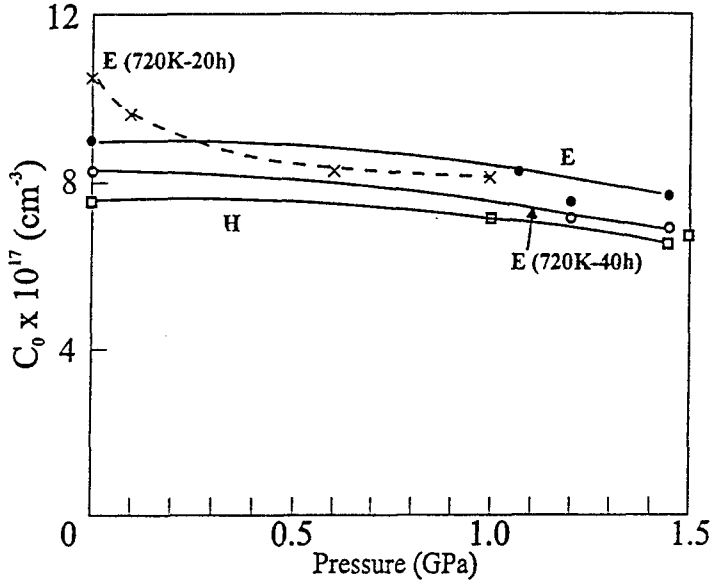

Fig. 5. Dependence of c_0 on HP for E and H samples, as - grown and pre - annealed at 720 K and afterwards treated at 720 K / 870 K - HP for 10 h. Circles and squares concern samples treated at 720 K - HP, while crosses (dashed line) - of sample treated at 870 K - HP. Marks on the left axis correspond to HP = 10^7 Pa.

with Table 1). The HT - HP treatment results in HP - stimulated creation of TD's, even in the case of the G sample with comparatively high „initial" concentration of TD's, introduced by very prolonged (170 h) pre - annealing at 720K under atmospheric pressure (Fig. 3). Similar HP - induced increase of the TD's concentration was stated for the G samples subjected to pre - annealing at 720K - 10^5 Pa for 96 h.
The samples pre - annealed at 920 K and especially at 1000 - 1020 K indicate markedly lower rate of HP - induced TD's creation; the TD's concentration increases, however, with HP for the samples treated at 720 K - HP (Figs 3, 4).
The samples subjected to comparatively short - time (2 - 4 h) pre - annealing at even higher temperatures (1320 K and 1420 K) still indicate distinct HP - induced increase of N_e. For example, the B sample pre - annealed at 1420 K - 10^5 Pa for 2 h (which resulted in creation of defects: $d_{SF} = 9x10^3$ cm^{-2}, $d_{SPD} = 1.3x10^3$ cm^{-2}) indicate $N_e = 7x10^{14}$ cm^{-3} after the treatment at 720 K - 10^7 Pa for 6 h and $N_e = 1.4x10^{15}$ cm^{-3} after the treatment at 720 K - 1 GPa for 6 h.
The Cz-Si samples subjected to two - steps pre - annealing (the last step at 1320 - 1420 K) and so with markedly higher concentration of oxygen - related defects and decreased content of oxygen remaining still in the interstitial positions, do not indicate dependence of carrier concentration on HP and so creation of TD's is negligible (Table 5).

Table 5. Effect of treatment at 720 K - HP on E samples subjected to 2 - steps pre - annealing. $N_p(0.03)$ means hole concentration after treatment at 720 K - 0.03 GPa and N_p (1.1) - the same after treatment at 720 K - 1.08 GPa, both for 10 h. * means reference A sample (compare Table 1).

Pre-annealing [K, h]:	$c_o x10^{17}$, cm^{-3}	d_{SF}, cm^{-2}	$d_{PDC}+d_{SPD}$, cm^{-2}	N_p (0.03), cm^{-3}	N_p (1.1), cm^{-3}
920K20h+1420K20h	6.3	-	$2.5x10^6$	$2.6x10^{15}$	$2.3x10^{15}$
920K20h+1320K20h	6.0	-	$3x10^5$	$1.5x10^{15}$	$1.5x10^{15}$
920K40h+1320K20h	5.4	$1.5x10^6$	$3x10^3$	$1.6x10^{15}$	$1.6x10^{15}$
1000K20h+1320K20h	3.2	$2.5x10^6$	$1.5x10^6$	$1.5x10^{15}$	$1.5x10^{15}$
A*(1000K - 20h)*	4.9*			$N_n=1.6x10^{14}$*	$N_n=2.6x10^{14}$*

4. DISCUSSION AND CONCLUSIONS

Cz-Si samples investigated in this study were subjected to pre - annealing at 720 - 1420 K, typical for creation of different oxygen - related defects, and to the HT - HP treatment at 670 -720 K, typical for generating of TD's. Total pre - annealing time was up to 170 h, whereas duration of the HT - HP treatment - up to 20 h. The pressure - stimulated creation of thermal donors[3,4] was confirmed in present work for the as - grown samples (Figs 1, 2).
The rate of creation of „HP - induced" TD's is dependent and, in the first approximation, proportional (Fig. 1) to the interstitial oxygen concentration[2,7]. However, by comparing the ΔN_e dependence on HP for the initially n-type (B and C) and p-type samples (A and D) in pairs of the similar c_o value (A with B and C with D in Fig. 1, F with G in Fig. 2), as well as of the data in Table 2, one can conclude that ΔN_e is definitely dependent also on other, except the concentration of interstitial oxygen, factors. Most probably just different non - uniformity in the O_i distribution[10 -12] and so the presence of cloud - like oxygen clusters are responsible for dependence of the TD's generation rate[7] also on the sample origin as well as on particular sample batch (Figs 1 and 2, Table 2). Just the HP - induced activation of initially existing structural irregularities, that act at HT - HP as the nucleation centres for the growth of oxygen clusters exhibiting donor activity[4,7] can be responsible for stress - stimulated creation of TD's[7].
Pre - annealing of Cz-Si at 720 - 1020 K at atmospheric pressure resulted in creation of some structural defects (Table 3) as well as of „ambient - pressure" TD's and ND's. The treatment of such samples at 670 - 720 K - HP produced TD's in astonishingly high concentrations (Figs 3, 4, Table 4). It concerns even the sample pre - annealed for 170 h (the TD's concentration has been reported to be saturated or even decreasing with time of annealing[13] in the case of prolonged annealing at 10^5 Pa). It suggests that the nature of the „HP - induced" TD's is different[5] from that for TD's created at 10^5 Pa. Most possibly, both the „ambient - pressure" TD's and the „HP - induced" TD's are created simultaneously but at different proportions at 670 - 720 K - HP. The generation of „HP - induced" TD's seems to be clearly related to structural irregularities present in the HP - treated oxygen - containing Cz-Si samples. Pre-annealing of Cz-Si at 720 - 920 K seemingly does not result markedly in decrease of the concentration of such precursors of TD's (the markedly HP - induced increase of N_e was still observed in such materials - Figs 3, 4 and Table 4).

Pre - annealing at higher (starting from about 920 K) temperatures, and especially 2 - steps pre - annealing (resulting in creation of numerous extended defects - Table 5) follow in much decreased rate of creation of the „HP - induced" TD's (Fig. 4) or even in practical absence of their creation (Table 5). Decrease of interstitial oxygen concentration (Fig. 5) resulting from 2 - steps pre - annealing can not explain this effect because the sample A pre - annealed at 1000 K, with $c_o = 4.9 \times 10^{17}$ cm^{-3} (Table 5) indicates creation of TD's while the samples with distinctly higher c_o (5.4 - 6.3x10^{17} cm^{-3}) but subjected to 2 - steps pre - annealing do not exhibit an effect of the HP - induced TD's generation.
It means that pre - annealing at about 1000 K and, especially that performed at 2 steps (the second step at 1230 - 1420 K), result in such changes of the state of O_i in Cz-Si that the HP - induced generation of TD's becomes to be practically suppressed. It is reasonable to suppose that the clouds / clusters of oxygen interstitials which are believed[7] to be responsible for creation of HP - related TD's, are disappearing at > 1000 K because of O_i precipitation as well as of Ostwald ripening effect. Similar effect of suppressed generation of the „ambient pressure" TD's has also been reported for Cz-Si containing defects created by annealing at up to 1370 K under atmospheric pressure[14].
Unambiguous determination of the nature of the „HP - induced" TD's deserves extended future research.

ACKNOWLEDGEMENTS

Author thanks Dr W.Jung, Dr T.Przeslawski, Mr T.Koska and Mr M.Prujszczyk from the Institute of Electron Technology as well as m. sc. H.B. Surma from IEMT, Warsaw for sample preparation and some measurements. This work has been supported in part by the Polish Committee for Scientific Research, grant no. 7T08A 05717.

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